

CATALYTIC CONVERSION OF METHANE TO METHANOL,  
FORMALDEHYDE AND HIGHER HYDROCARBONS

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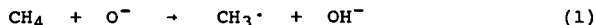
INTRODUCTION

By suitably choosing the catalyst and oxidant it is possible to direct the conversion of methane either to oxygenated products (HCHO and CH<sub>3</sub>OH) or hydrocarbons (mainly C<sub>2</sub>H<sub>4</sub>). High selectivities to methanol and formaldehyde have been achieved only at low conversion levels and only using nitrous oxide as the oxidant (1,2). Considerably more progress, however, has been made in the oxidative coupling of methane to form ethane and ethylene (C<sub>2</sub> products) (3-8). The purpose of this paper is to show that both formation of oxygenates and C<sub>2</sub> products occur by a common intermediate, namely the CH<sub>3</sub>· radical, which in one case reacts with the surface to form methoxide ions, and in the other reacts mainly in the gas phase to form ethane.

CONVERSION TO OXYGENATES

Molybdena supported on silica is moderately active and selective for the catalytic conversion of CH<sub>4</sub> to CH<sub>3</sub>OH and HCHO when N<sub>2</sub>O is used as the oxidant as indicated by the results of Table I (1). Up to ca. 2% conversion very high combined selectivities to CH<sub>3</sub>OH and HCHO were obtained, but at 6% conversion the selectivities to the desired oxygenates were decreased considerably. With O<sub>2</sub> as the oxidant the results were considerably poorer.

Although this system holds little promise as a practical catalyst, it does provide insight into possible means of activating CH<sub>4</sub> and following the chemistry of surface intermediates. This study, for example, points to the role of thermally generated O<sup>-</sup> ions in the activation of methane. Previous work by Bohme and Fehsenfeld (9) have shown that gas phase O<sup>-</sup> ions are very effective in the abstraction of hydrogen atom from simple alkanes via the reaction



Likewise, methyl radicals are formed on Mo<sup>VI</sup>/SiO<sub>2</sub> via the photochemical reactions



and their EPR spectra are shown in Figure 1b (1,10). Of more importance in catalysis, O<sup>-</sup> may be formed by the thermal reaction of Mo<sup>V</sup>/SiO<sub>2</sub> with N<sub>2</sub>O, and CH<sub>4</sub> reacts with these oxygen ions at temperatures as low as -196°C. The resulting CH<sub>3</sub>· radicals are shown in Figure 1a.

Infrared results (Figure 2) suggest that these  $\text{CH}_3\cdot$  radicals react with the molybdena surface via reductive addition to form methoxide ions. It is known from extensive work on the partial oxidation of methanol over supported and unsupported molybdena that methoxide ions are intermediates in the formation of formaldehyde. In the presence of water these molybdenum alkoxide ions react to form methanol. Thus, the partial oxidation of methane to oxygenates may be understood by the catalytic cycle depicted in Scheme I. In addition to the selective cycle one must also consider the possibility of a two-electron reaction with  $\text{N}_2\text{O}$  to form oxide ions. A molecule of  $\text{CH}_4$  would then have to be consumed in a nonselective manner to reduce  $\text{Mo}^{\text{VI}}$  back to  $\text{Mo}^{\text{V}}$ . In principle the two-electron transfer could be minimized by dispersing the Mo as a dimer on the surface and by avoiding the reduction of this molybdenum to the IV oxidation state.

#### OXIDATIVE COUPLING

When methyl radicals are formed on oxides which contain no reducible metal ions, then the formation of methoxide ions is limited and the radicals have adequate lifetimes either to couple on the surface or to desorb into the gas phase. Several of the more active and selective catalysts for the oxidative dimerization of methane are listed in Table II, where it is apparent that the steady state yields of  $\text{C}_2$  products may reach 25%. The starting materials are given in the table and under reaction conditions the working catalyst are mainly metal oxides which are extensively covered by alkali metal carbonates. These carbonates probably serve, in part, to prevent the formation of methoxide ions on oxides such as  $\text{ZnO}$  and  $\text{Mg}_6\text{MnO}_8$ .

In addition, alkali metal ions may yield specific centers which are capable of forming methyl radicals. For example, with the  $\text{Li}^+/\text{MgO}$ , and  $\text{Na}^+/\text{CaO}$  catalysts centers of the type  $[\text{Li}^+\text{O}^-]$  and  $[\text{Na}^+\text{O}^-]$  serve as sources of  $\text{O}^-$  ions, which activate methane as described in the previous section (3,5). There is increasing evidence that at reaction temperatures greater than  $750^\circ\text{C}$ , the alkali metal carbonates partially decompose to form their respective oxides and that the oxides themselves are able to activate methane. This is particularly true for  $\text{Na}_2\text{O}_2$ , which is the most stable oxide of sodium (13).

On the crystal faces of closed shell oxides, of which  $\text{MgO}$  is an example, the bonding of  $\text{CH}_3\cdot$  radicals is weak (14), and therefore it is not surprising that the radicals emanate into the gas phase where coupling occurs. It has been demonstrated that over a  $\text{Li}^+/\text{MgO}$  catalyst >40% of the  $\text{C}_2$  products may be formed by such gas phase coupling reactions (15,16). Unfortunately, in the presence of molecular oxygen other gas phase radical reactions may occur which ultimately result in the formation of  $\text{CO}_2$ . Similarly,  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_4$  may be oxidized both heterogeneously and homogeneously which limits  $\text{C}_2$  yields to ca. 25%.

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Table I. Conversion and Selectivity during Methane Oxidation<sup>a,b</sup>

T, °C	conven, %	selectivity, %			
		HCHO	CH <sub>3</sub> OH	CO	CO <sub>2</sub>
550	1.6	79.5	20.5		
560	1.9	80.1	19.9		
570	2.9	64.3	13.8	19.1	2.8
580	4.0	58.8	10.0	27.7	3.4
594	6.0	49.5	7.8	38.1	4.6

<sup>a</sup>1.0 g of Mo/Cab-O-Sil, P<sub>CH<sub>4</sub></sub> = 75 torr, P<sub>N<sub>2</sub>O</sub> = 280 torr, P<sub>H<sub>2</sub>O</sub> = 260 torr, F = 1.33 mL/s.

<sup>b</sup>Ref. 1.

Table II. Oxidative Coupling of Methane Over Promoted Metal Oxide Catalysts

Catalyst	Temp, °C	CH <sub>4</sub> Conv, %	C <sub>2</sub> Sel, %	C <sub>2</sub> Yield %	Ref.
Li <sub>2</sub> CO <sub>3</sub> /MgO	720	43	45	19.4	1
Li <sub>2</sub> CO <sub>3</sub> /Sm <sub>2</sub> O <sub>3</sub>	750	38	54	20.7	6
NaNO <sub>3</sub> /MgO	800	39	57	22.4	7
Li <sub>2</sub> CO <sub>3</sub> /ZnO	740	36	67	23.9	4
Na <sub>2</sub> CO <sub>3</sub> /CaO	725	33	45	14.8	5
NaMnO <sub>4</sub> /MgO	925	22	70	15.4	8

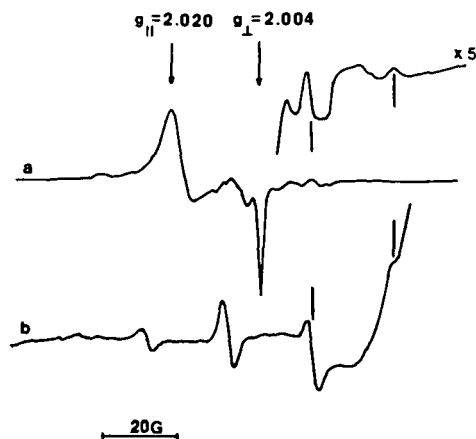


Figure 1. EPR spectra of methyl radicals: (a) after reaction of  $\text{CH}_4$  with  $\text{O}^-$  on  $\text{Mo/SiO}_2$ ; (b) after UV irradiation of oxidized  $\text{Mo/SiO}_2$  in the presence of  $\text{CH}_4$ . Reactions were carried out and spectra recorded with the sample at  $-196^\circ\text{C}$ . (Ref. 1)

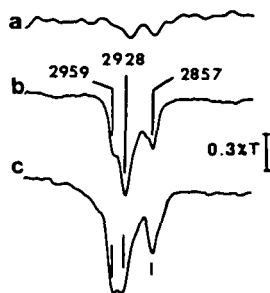
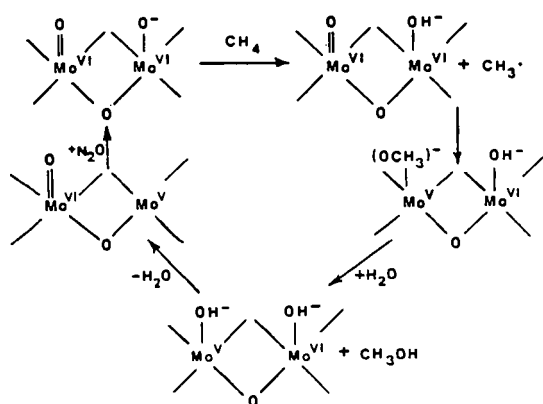
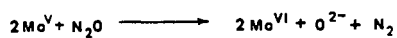
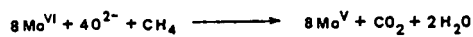


Figure 2. Infrared spectra of methoxide ions on  $\text{Mo/SiO}_2$ : (a) background after reduction of catalyst in  $\text{CO}$ , followed by adsorption of  $\text{N}_2\text{O}$  and evacuation; (b) after subsequent adsorption of  $\text{CH}_4$  and evacuation; (c) after adsorption of  $\text{CH}_3\text{OH}$  and evacuation. (Ref. 1)



SCHEME 1